Analysis of Alloying Elements in Various Alloys and Determination of Small Amounts of Elements by X-Ray Fluorescent Spectroscopy

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Synopsis

In order to analyse alloying elements in various alloys by x-ray fluorescent spectroscopy, a correction equation for the background of overlapped spectral lines was proposed. This equation was applied to Sn Kα line and Sb Kα line from Sn-Sb alloy or Cr Kβ line and Mn K$_\alpha$ line from special steels. On the other hand, it was recognized that the equation $I_a = K_a I_0 W_a / \Sigma \mu_a^q W_a$ was useful for the estimation of influence of accompanying element, and this was ensured with Fe-Cr alloy, Sn-Pb alloy and some binary mixtures. Modifying this equation by the standard addition method, the x-ray fluorescent spectroscopic methods with 1 or 2 compensative references were established.

The simultaneous determination of alloy film thickness and its composition with x-ray fluorescent spectroscopy which had not hitherto been attempted was studied with Ni-Fe alloy film, and an experimental equation for the simultaneous determination was obtained. In this case, the influence of the element in backing materials was recognized, which might be called the absorption edge effect. This effect could be utilized to increase the sensitivity of the determination of a small amount of elements.

I. Introduction

Many works have been reported on the x-ray fluorescent spectroscopic analysis. Especially, the application of the method has been done to special steels, cement, and organic materials. In earlier times it had been difficult to detect small amounts of elements or to analyse light elements by this method, but nowadays these difficult points have been overcome one by one with many investigations together with the improvements of instruments. Many studies have been reported on the interelement effect, on the preparation of samples, on the measuring errors and backgrounds. For the analyses of various alloys, the rapidity and the non-destructivity are characteristic of this method and therefore, it is very available for refractory materials. On the other hand, in some cases, for example, like ore or ferroalloy samples, the measuring samples must be prepared in homogeneous form (liquid or powder) in order to get a good reproducibility. Since 1956 the rapid analyses of various alloys and the determination of small amounts of elements have been studied in the institute. In the present report, these studies will be described together with some ones already reported.

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* The **1243rd** report of the Research Institute for Iron, Steel and Other Metals.

II. Calibration curve method

The calibration curve method is the most usual in the x-ray fluorescent spectroscopic analysis, and has been applied to the analyses of binary alloys[1][2], ternary alloys, special steels[3][4][5] and to the determination of small amounts of elements[6]. According to the sample preparation, this method is divided into the non-destructive and the destructive technique. Most parts of the present report will describe the non-destructive method from the situation of the study of rapid analytical method. In the non-destructive analysis, the calibration curve does not show linearity between the concentration of the element to be analyzed and its x-ray intensity, but when the concentration range is small or in a special case, the linear calibration curve can be obtained.

At first, in Fig. 1 the calibration curves for tin-lead and tin-antimony binary alloys[2] are shown in whole concentration range. In this case, the excitation conditions were as follows: 40kV, 15 mA, Sn Kα line, Sb Kα line and Pb Lα line; G.E. XRD-5 X-Ray Spectrometer with lithium fluoride analyzer, 0.01 inch space sollar slit and 2 SPG Detector. In the following experiments this instrument was also used. With the same condition the calibration curve for tin-antimony-lead

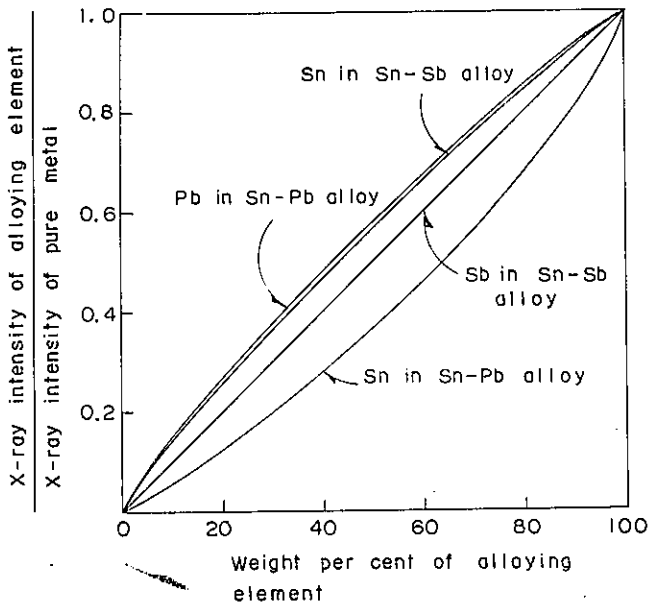

Fig. 1. Calibration curves for Sn-Sb alloy and Sn-Pb alloy.

(1) K. Hirokawa, J. Japan Inst. Metals, **23** (1959), 376.
(2) K. Hirokawa, Sci. Rep. RITU, **A 13** (1961), 271.
(3) K. Hirokawa, Sci. Rep. RITU, **A 14** (1962), 278.
(4) K. Hirokawa and H. Gotô, Sci. Rep. RITU, **A14** (1962), 294.
(5) K. Hirokawa, T. Shimanuki and H. Gotô, Sci. Rep. RITU, **A 15** (1963), 124.
(6) K. Hirokawa, Sci. Rep. RITU, **A 13** (1961), 263.

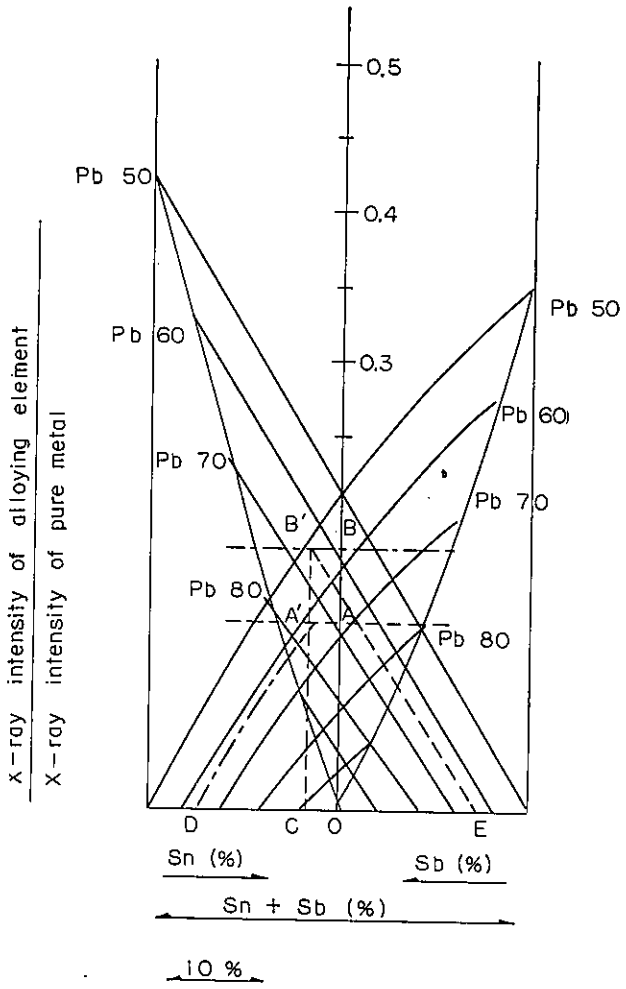

Fig. 2 Calibration curve for Sn-Sb-Pb alloy

(over 50 per cent of lead) was prepared, which is shown in Fig. 2. The procedure of applying this curve is as follows: With a tin-antimony-lead alloy an x-ray intensity ratio of tin was obtained as A, and that of antimony as B. Horizontal line parallel to abscissa showing concentration is drawn through A and B, and then a rule is moved in parallel to the ordinate showing the intensity ratio until the crossing of two parallel lines comes to the point of the same concentration range of lead. These points are designated as A' and B'. The point at which the extended line A'-B' crosses the abscissa is taken as C, and the point at which the line extending from A' in parallel to the curve of tin crosses the abscissa is taken as D. The distance C-D indicates the content of tin and the distance C-E obtained similarly to the curve of antimony indicates the content of antimony. The lead content can approximately be assumed from the position of A' or B', and the

content of each element can easily be determined. In these cases Sn $K\alpha$ line and Sb $K\alpha$ line were used for the tin-antimony and the tin-antimony-lead alloy, but the separation of both lines was not sufficient. Therefore, the following equation was used to correct overlapped spectral lines. When the true x-ray intensity of Sn $K\alpha$ line was denoted by $I_{Sn}{}^{T}$ and that of antimony by $I_{Sb}{}^{T}$, the x-ray intensity of Sn $K\alpha$ line measured from tin antimony or from tin-antimony-lead alloy was $I_{Sn}{}^{C}$ and that of antimony was $I_{Sb}{}^{C}$. The x-ray intensity at the peak of Sn $K\alpha$ line with pure tin metal was designated as $I_{Sn}{}^{P}$ and the x-ray intensity of Sb $K\alpha$ line with antimony metal at the same place was designated as $I_{Sb}{}^{F}$. Similarly, the x-ray intensity at the peak of Sb $K\alpha$ with pure antimony metal was designated as $I_{Sb}{}^{P}$ and the x-ray intensity of Sn $K\alpha$ with tin metal at the same place was designated as $I_{Sn}{}^{F}$.

$$\left.\begin{aligned} I_{Sn}{}^{T} &= \frac{I_{Sn}{}^{C} - I_{Sb}{}^{C}\dfrac{I_{Sb}{}^{F}}{I_{Sb}{}^{P}}}{1 - \dfrac{I_{Sn}{}^{F}\cdot I_{Sb}{}^{F}}{I_{Sn}{}^{P}\cdot I_{Sb}{}^{F}}} = \frac{I_{Sn}{}^{C} - 0.11\, I_{Sb}{}^{C}}{0.996} \\ I_{Sb}{}^{T} &= \frac{I_{Sb}{}^{C} - I_{Sn}{}^{C}\dfrac{I_{Sn}{}^{F}}{I_{Sn}{}^{P}}}{1 - \dfrac{I_{Sn}{}^{F}\cdot I_{Sb}{}^{F}}{I_{Sn}{}^{P}\cdot I_{Sb}{}^{F}}} = \frac{I_{Sb}{}^{C} - 0.036\, I_{Sn}{}^{C}}{0.996} \end{aligned}\right\} \quad (1)$$

Then the correction equation (1) was obtained for tin-antimony or tin-antimony-lead alloy. With this equation the background of overlapped peak was corrected and the true intensities $I_{Sb}{}^{T}$ and $I_{Sn}{}^{T}$ are obtained. The same technique was also applied to the determination of manganese and chromium in special steels and satisfactory results were obtained. In this case, Mn Kα line and Cr Kβ line were used and the background correction equation (2) was obtained. The calibration curve with Eq. (2) and the analytical results using this technique are shown in Fig. 3 and Table 1, respectively. (the excitation condition: 45 kV and 15 mA)

$$I_{Mn}{}^{T} = \frac{I_{Mn}{}^{C} - 0.226\, I_{Cr}{}^{C}}{0.951}, \qquad I_{Cr}{}^{T} = \frac{I_{Cr}{}^{C} - 0.218\, I_{Mn}{}^{C}}{0.951} \quad (2)$$

The calibration curve method was applied not only to metal or to alloy samples with the non-destructive technique, but also to fused sample or to solution sample, for example, iron in iron ore, manganese in ferromanganese, or chromium in ferro-chromium[5][7]. In the case of fusion or of solution method, the interelement effect decreases with the matrix dilution effect, and the calibration curve with good linearity can be obtained over a wide range of concentration. Otherwise, this method is not non-destructive and therefore, the internal standard can be utilized. In Fig. 4 the example of calibration curve for iron in iron ore with cobalt internal standard in phosphoric acid solution is shown. In fusion method or in solution

(7) H. Goto, K. Hirokawa and F. Maeda, Japan Analyst, **13** (1964), 402.

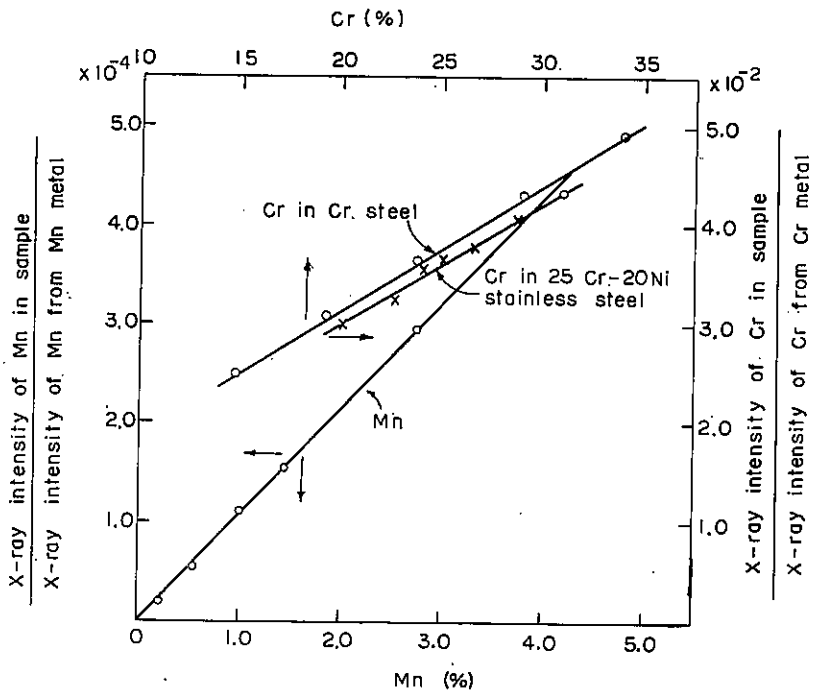

Fig. 3. Calibration curve for Mn and Cr in stainless steel.

Table 1. Determination of Mn and Cr in stainless steels.

Sample	Mn (%)		Cr (%)		Others (%)
	X-ray	Chem.	X-ray	Chem.	
TK 6	1.44	1.43	24.40	24.29	Si : 1.83, Ni : 20.58
L 229	1.04	1.00	24.70	24.66	Ni : 22.49
L 210	0.53	0.52	24.48	24.91	Ni : 23.00
L 227	4.14	4.18	24.85	25.22	Ni : 21.13
L 224	2.78	2.70	26.28	26.29	Ni : 21.81
L 228	—	—	22.48	22.26	Si : 0.11, Ni : 21.57
L 188	—	—	24.00	23.79	Si : 0.81, Ni : 21.44
L 189	—	—	25.18	24.88	Si : 2.39, Ni : 20.93
L 109	—	—	24.60	24.54	Si : 2.53, Ni - 22.18
L 191	—	—	25.42	24.76	Si : 1.93, Ni : 20.05
C 30	—	—	18.40	18.38	
C 26	0.35	0.32	18.20	18.23	

method, however, the effect of dissolving material on the x-ray intensity of element to be analyzed must be considered, and in the powder sample method the problem of the variation of x-ray intensity with the variation of particle size also comes in together with the interelement effect.

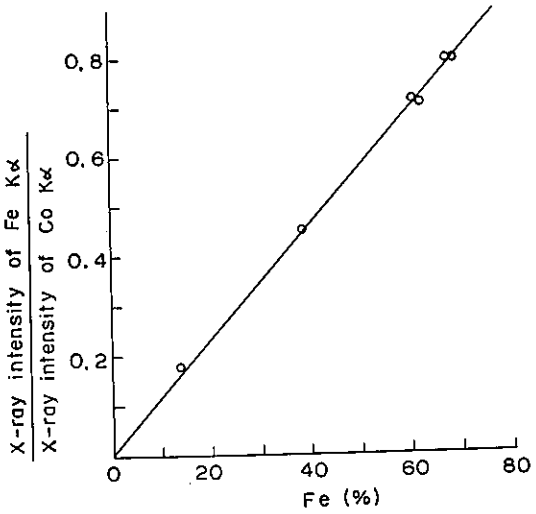

Fig. 4. Calibration curve of iron in iron ore in phosphoric acid solution with internal standard of cobalt.

III. One simple method for the estimation of interelement effect and its application

In x-ray fluorescent spectroscopy the interelement effect must be considered as described in the section II. On the interelement effect, theoretical researches were carried out by Sherman[8] and others with computers[9][10], and the experimental[11][10] studies have also been reported. In the present report, the equation $I_a=K_aI_0W_a/\Sigma\mu_a^aW_a$, which shows the relation between x-ray intensity of element (a) and its weight fraction, is used as a starting point to estimate the interelement effect, and the mass absorption coefficient is introduced into the term of μ_a^a. Under definite conditions it was recognized that the K_a value was nearly constant in the concentration range of about 10～20 per cent of alloying element with the use of the mass absorption coefficient and with the I_a value measured with the known W_a of a binary alloy. Then the effect of the third element on the binary alloy could be semiquantitatively estimated with the equation.[12] In other reports it has been shown that the act of mass absorption coefficients is very effective[13][14]. Therefore, it was considered that the interelement effect might be easily calculated with the use of mass absorption coefficient under

(8) J. Sherman, Spectrochim. Acta, **7** (1955), 283.
(9) W. Marti, Spectrochim. Acta, **18** (1962), 1499.
H.J. Lucas-Tooth et al., Metallurgia, **64** (1961), 149.
(10) H.J. Beatti and R.M. Brissey, Anal. Chem., **26** (1954), 980.
(11) K. Hirokawa, Sci. Rep. RITU, A **13** (1961), 279.
(12) K. Hirokawa, Sci. Rep. RITU, A **14** (1962), 288.
(13) M. Sugimoto, Japan Analyst, **12** (1963), 475.
(14) T. Shiraiwa et al. reported in Conference of the Japan Institute of Metals, Tokyo, 1964.

the condition of the nearly monochromatic primary x-ray that was obtained by controlling the excitation voltage. When the calculation is possible, the preparation of the calibration curve may be possible without obtaining the parameter such as K_a from binary alloys or other standard samples, and with this calibration curve some alloys may be analyzed. From this situation some experiments were carried out with chromium-iron alloy, nickel-iron alloy and the mixture of zinc oxide-chromium oxide[15].

1. Principle

The following equation (3) was used:

$$I_a = \frac{K_a I_0 W_a}{\Sigma \mu_a^a W_a}, \tag{3}$$

where W_a is the weight fraction, μ_a^a the mass absorption coefficient, I_0 the intensity of the primary x-ray, and K_a a constant. From Eq. (3) the ratio of the x-ray intensity of the element A in a binary alloy (AB) to that in the metal (AA) I_{AB}/I_{AA} was calculated. In this intensity ratio the geometry of the instrument G. E. XRD-5, and μ values for the primary x-ray μ_i and for the fluorescent x-ray μ_f were introduced. Then the following equation (4) was obtained.

$$\frac{I_{AB}}{I_{AA}} = \frac{(\mu_i + \sqrt{3}\,\mu_f)_A^A W_A}{(\mu_i + \sqrt{3}\,\mu_f)_A^A W_A + (\mu_i + \sqrt{3}\,\mu_f)_B^A W_B}, \tag{4}$$

where μ_i is the mass absorption coefficient for primary x-ray, μ_f the mass absorption coefficient for secondary x-ray (fluorescent x-ray), $(\mu_i)_A^A$ the mass absorption coefficient of element A for primary x-ray, $(\mu_i)_B^A$ the mass absorption coefficient of element B which is accompanied with element A for primary x-ray, and $(\mu_f)_A^A$ and $(\mu_f)_B^A$ the mass absorption coefficients of those for secondary x-ray. The primary x-ray which is dependent on μ_i has the wavelength ranging from the minimum value λ_0 at the definite excitation voltage to the absorption edge of the element to be analyzed. In the present experiment, however, the wavelength of the primary x-ray was controlled as follows: from the Daue-Hunt's law the minimum wavelength of the primary x-ray at the definite voltage was $\lambda_0 = 12.40/\mathrm{kV}$ and the wavelength of the maximum intensity was $\lambda_{max} = 1.5\lambda_0$. Therefore, the excitation voltage was controlled such as the wavelength of maximum intensity λ_{max} to come near the wavelength of the absorption edge of the element to be analyzed. The term μ_i was used as the maximum mass absorption coefficient at the wavelength of the absorption edge, and calculated from the equation $\mu = b\lambda^k$.

2. The investigation with some binary alloys and binary mixtures

In Fig. 5 the mass absorption coefficient (μ) of chromium, iron, nickel, zinc and

(15) H. Gotô and K. Hirokawa, reported in the Conference of the Japan Institute of Metals, Tokyo, 1964

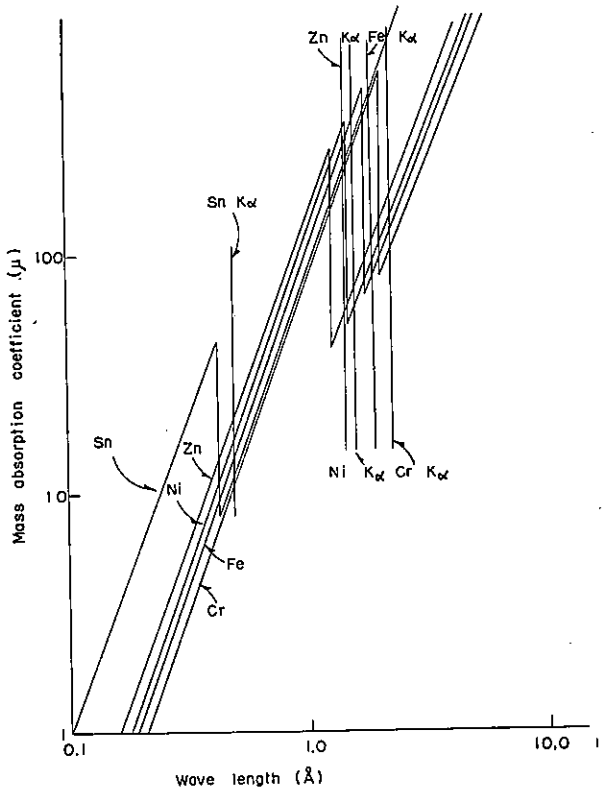

Fig. 5. The position of spectral lines of Cr, Fe. Ni, Zn and Sn and their mass absorption coefficient

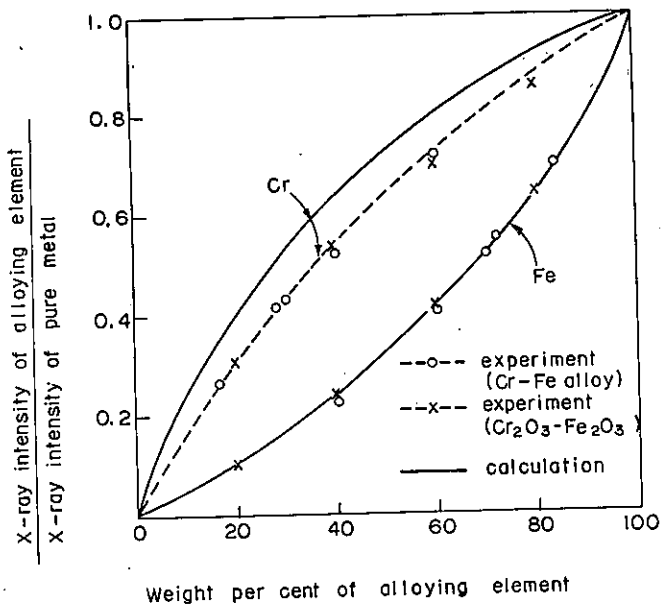

Fig. 6. Calibration curve for Cr-Fe alloy with calculation and experiment.

Table 2. b and k value for chromium, iron, nickel and zinc.

Element	Cr		Fe		Ni		Zn	
Wave length	<2.07	>2.07	<1.74	>1.74	>1.49	>1.49	<1.28	>1.28
b	80.3	9.40	100	12.5	120	15.5	138	17.9
k	2.76	2.71	2.76	2.67	2.75	2.71	2.68	2.72

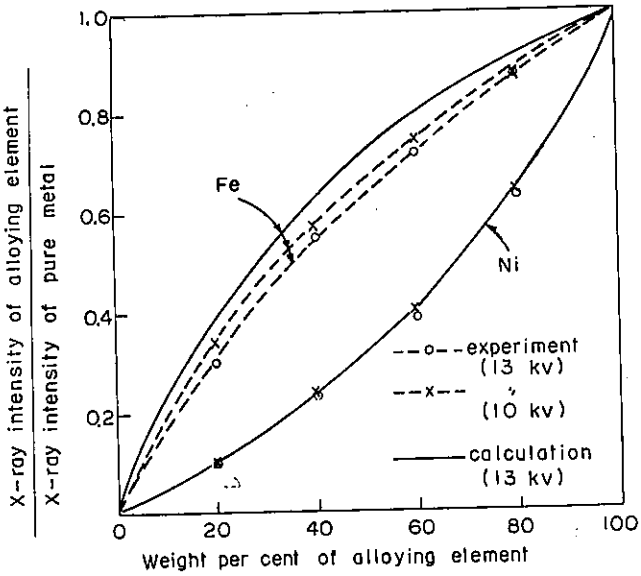

Fig. 7. Calibration curve for Ni-Fe alloy with calculation and experiment.

tin are shown with their $K\alpha$ spectral lines. In the nickel-iron alloy the enhancement effect of nickel on iron is supposed. Similarly, the same effect is also considered on chromium in chromium-iron alloy and in chromium oxide-iron oxide mixture. Now, the values k and b in Table 2 were used for the equation $\mu=b\lambda^k$, and the values of (μ_i) for each element were calculated. With these values and the values of (μ_f), the calibration curves were prepared from Eq. (5). The calculated and the experimental values for iron-chromium alloy and for iron oxide-chromium oxide mixture are shown in Fig. 6. In this case, the selected excitation potential was 10kV (15 mA) in order to bring the wavelength of the maximum x-ray intensity near the absorption edge wavelength. Similarly, the examples for some binary alloys and binary mixtures are shown in Figs. 7, 8 and 9. From these results, it was recognized that when there was no secondary enhancement effect, the calibration value agreed well with the experimental value under the definite conditions. Therefore, in some cases, the composition of binary alloys or of mixtures can be calculated with the x-ray intensity ratios which are obtained under the definite conditions. When there is the secondary or more enhancement effects,

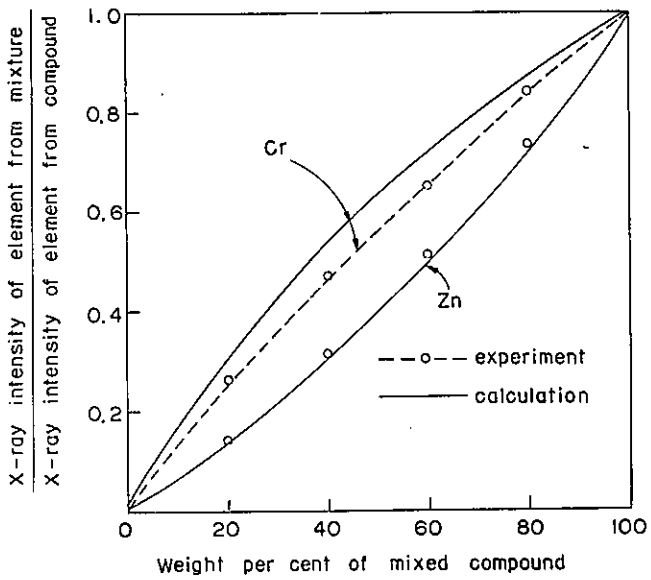

Fig. 8. Calibration curve for Cr_2O_3-ZnO mixture with calculation and experiment.

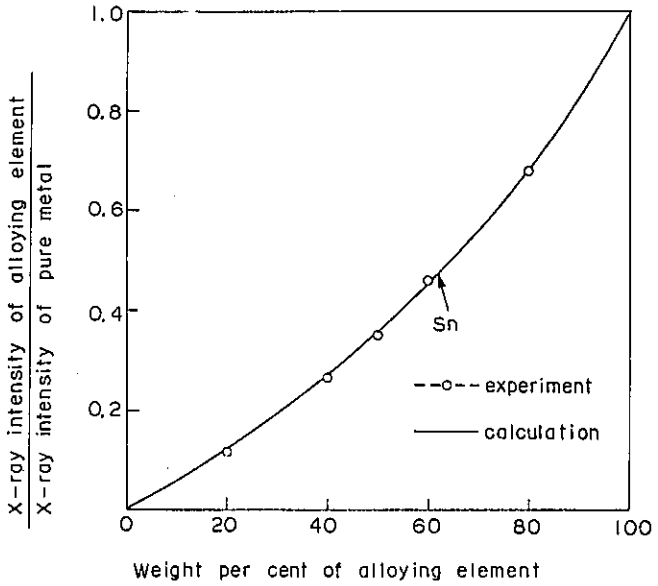

Fig. 9. Calibration curve for Sn-Pb alloy with calculation and experiment.

it is necessary to apply secondary or more corrections. Recently, on the correction of secondary enhancement effect, the application of computers has also been reported[14].

IV. Determination of alloying elements with one or two compensative references[16][17]

These methods are rapid non-destructive and simple. The available equations for these methods were derived from Eq. (3), and the terms showing the influence of accompanying elements were eliminated. Therefore, these methods could be applied without many standard samples or without using some parameters which had been previously prepared with many experiments. These equations were, however, introduced with the supposition that the existence ratio of accompanying elements was nearly constant and therefore, for binary alloys or for one series of actual samples, these equations were very available.

1. Single compensative reference method[17]

This method is available in the following cases. For example, the sample which should be analyzed is kept and there is only one compensative reference sample which contains the same component as that sample and its composition is known. In this case the principle started with Eq. (3), and the supposition that the mass absorption coefficients of alloying elements were similar to one another such as lead-bismuth alloy, nickel-cobalt alloy ($\mu_A{}^A=\mu_B{}^A=\mu_B{}^B\cdots$) was introduced into this equation. Then the following equation group for the analysis was obtained.

$$W_A \fallingdotseq \frac{\frac{I_A}{I_a}w_a}{\Sigma\frac{I_A}{I_a}w_a}, \quad W_B \fallingdotseq \frac{\frac{I_B}{I_b}w_b}{\Sigma\frac{I_A}{I_a}w_a}, \cdots\cdots, \tag{5}$$

where ω_a is the weight fraction of element a in standard reference, and I_a its x-ray intensity. The example of results with this equation is shown in Table 3. This

Table 3. Determination of alloying elements in lead-antimony and tin-lead-antimony alloys*

Sample	Sb (%)		Sn (%)		cf.
	Chem.	X-ray	Chem.	X-ray	
SSb 10	8.07	7.99	residue	92.01	Sn-Sb alloy, Standard sample: Sb: 26.28% Sn: residue
SSb 40	38.16	37.72	〃	62.30	
SSb 45	54.52	54.16	〃	45.84	
SSb 5	5.28	5.10	〃	94.91	
b 5 n 5	5.72	5.69	5.54	5.01	Sh-Sb-Pb alloy, Standard sample: Sn: 9.40% Sb: 19.76% pb: residue
b 1 n 5	10.86	10.06	4.69	5.06	
b 5 n25	5.16	5.75	24.99	23.24	
b15 n 5	5.09	6.25	15.33	14.64	

* Excitation source : 40 kV 15 mA

(16) K. Hirokawa and H. Gotô, Z. anal. Chem., **185** (1962), 124.
(17) K. Hirokawa and H. Gotô, Z. anal. Chem., **193** (1963), 346.

method can only be applied to a few binary or ternary alloys, but it is very convenient for some alloys because of its rapidity.

2. The method with two compensative references[16]

This method has no necessity of measuring the x-ray intensity of all alloying element as the previous method, and can apply not only to binary alloy but also to actual samples, solution samples and powder samples. The principle of this method was developed by introducing the idea of the standard addition method into Eq. (3), and two useful equations were obtained for this method. One is Eq. (6). In this case, as the reference standard one pure material and one known sample containing the same components as unknown sample were used.

$$W_x = \frac{w_a\left(\frac{I_A}{I_a} - 1\right)}{\frac{I_A}{I_a}(1 - w_a) + \frac{I_A}{I_a} w_a - 1}, \tag{6}$$

where I_A is the x-ray intensity of pure metal A (pure material of element to be analyzed), I_x the x-ray intensity of the element to be analyzed in a sample, I_a the x-ray intensity of the element to be analyzed in one reference standard sample, W_x the weight fraction of the element to be analyzed in a sample, and ω_a the weight fraction of this element in the standard.

On the other hand, when the pure material can not easily be obtained, another Eq. (7) can be applied. In this equation two known samples containing the same components as unknown sample are used as compensative references.

$$\frac{\frac{I_a}{I_b} \cdot \frac{w_b}{w_a} - 1}{w_b - w_a} = \frac{\frac{I_a}{I_x} \cdot \frac{W_x}{w_a} - 1}{W_x - w_a}, \tag{7}$$

where w_a and ω_b are the weight fractions of the element to be analyzed in the reference standard samples a and b, and I_a and I_b the x-ray intensities of them respectively. In Table 4, the results of Eqs. (6) and (7) applied to 25 per cent

Table 4. Results of the application of equations (6) and (7) to the determination of Ni and Cr-20 Ni stainless steel*

Sample	Ni (%)			Cr (%)		
	Chem. anal.	Eq. (6)	Fq. (7)	Chem. anal.	Eq. (6)	Eq. (7)
L 188	21.15	21.14	St	23.97	23.94	St
L 189	20.93	20.78	20.88	24.88	25.34	25.32
L 190	21.92	21.83	22.10	24.65	25.17	25.16
L 224	21.81	21.32	21.51	26.29	25.74	25.71
L 227	21.13	20.94	21.07	25.22	25.23	25.22
L 229	22.49	22.17	22.49	24.66	24.08	24.50
TK 6	20.58	20.68	20.76	24.29	24.27	24.30

* 24.77% Cr, 20.07% Ni stainless steel was used as standard; Ni K_α line and Cr K_α line used; excitation source: 30 kV, 10 mA.

chromium—20 per cent nickel stainless steels are shown. On the other hand, Eqs. (6) and (7) were able to be used not only for bulk metal samples but also for solution or powder samples. The results of Eq. (7) applied to manganese in ferromanganese and to chromium in ferrochromium[5] are shown, compared with the results of the calibration curve method, in Table 5. In this case, ferrochromium was fused with sodium peroxide and ferromanganese was dissolved with nitric acid, and turned into solution sample. As described before, the x-ray fluorescent spectroscopy with one or two reference standard methods were verified to be convenient to analyze bulk alloy samples, solution samples and powder samples.

Table 5. Comparison of the calibration curve method with the equation (7) method for manganse in ferromanganese and chromium in ferrochromium.***

Sample		Chemical analysis (%)	X-ray analysis			
			Intensity (c/s)	Calibration curve method (%)	Calculation results (%)	Dev. (%)
Cr in ferrochromium*	A	62.01	53.03	62.17	62.23	+0.06
	B	63.41	54.65	63.64	63.44	−0.20
	C	63.52	54.38	63.30	63.05	−0.25
	D	64.80	55.41	64.72	64.52	−0.20
Mn in ferromanganese**	A	76.06	365.6	76.43	76.43	0.00
	B	75.28	360.4	75.32	75.29	−0.04
	C	75.03	359.3	75.16	75.15	−0.01
	D	74.54	356.7	74.49	74.46	−0.03

* Standard sample used were 55.00% Cr and 65.00% Cr
** Standard sample used were 75.00% Mn and 80.00% Mn
*** Excitation source: 30 kV, 15 mA

V. Determination of small amount of element

1. Non-destructive method

In x-ray fluorescent spectroscopy, the determination of a small amount of elements with calibration curve method[6] was already reported. Iron, cadmium, arsenic, lead in zinc and arsenic, lead in tin and iron in titanium were examined. The calibration curves of these elements had good linearity, while these matrixes were almost simple and the concentration range of the element to be analyzed was below 1～2 per cent. With these calibration curves cadmium in zinc below 0.05 per cent, and iron in titanium below 0.05 per cent were determined. The application of Eq. (7) in IV–2 was also carried out to the determination of iron in zinc, and the results are shown in Table 6. In the case of the determination of impurities in nonferrous metals, it must be careful that some impurities, for example, iron, come onto the surface of the sample from the emery paper, and give rise to unexpected errors.

Table 6. Determination of iron in zinc.*

Chem. anal. (%)	X-ray anal. (%)	Difference (%)
0.16	0.15	−0.01
0.079	0.082	+0.003
0.002	0.0015	−0.0005

* Fe K_α line was used; iron content in standard samples are 0.35 per cent and 0.17 per cent: excitation source: 45 kV 15 mA.

2. Sample preparation with precipitation enrichment [18][19][20]

In order to increase the sensitivity and to avoid the interelement effect, the enrichment of the element to be analyzed through the separation from matrixes has been utilzied In this case, the precipitation with organic reagents was proposed. The elements which were enriched in the organometallic precipitate were irradiated with the primary x-ray, and the elements in the precipitates were analyzed. As the organic precipitant, Alizarine Blue was newly examined, and it was recognized that this reagent quantitatively precipitated with copper and iron at pH above 1.[21] For copper and iron below 200μg, the calibration curves were obtained with good linearity as shown in Fig. 10 (excitation condition: 40 kV, 15 mA), and they had no influence on each other. Therefore, it was possible to determine small amounts of iron and copper simultaneously from the same precipitate sample.[18] The results of determination of copper and iron in aluminium, zinc, manganese and

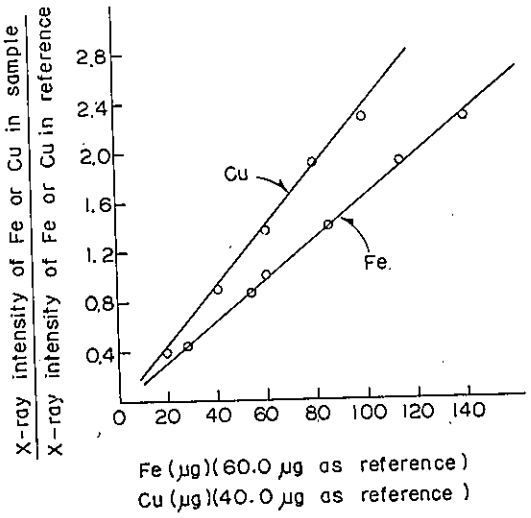

Fig. 10. Calibration curve of Fe and Cu with organometallic precipitation method

(18) K. Hirokawa and H. Gotô, Bull. Chem. Soc. Japan, **33** (1962), 961.
(19) K. Hirokawa and H. Gotô, Bull. Chem. Soc. Japan, **33** (1962), 964.
(20) H. Gotô, K. Hirokawa and F. Maeda reported in the Conference of Chemical Society of Japan, Tokyo, 1964.
(21) K. Hirokawa, Sci. Rep. RITU, **A 14** (1962), 112.

Table 7. Determination of copper and iron in aluminium, zinc, manganese and nickel.*

Sample	Sample taken (g)	Cu added (μg)	Cu analyzed (μg)	Cu recovered (μg)	Fe added (μg)	Fe analyzed (μg)	Fe recovered (μg)
Al	0.087	0.0 41.8	2.0 44.4	— 42.0	0.0 41.8	3.2 44.0	— 40.8
Zn	0.114	0.0 38.3	2.2 40.8	— 38.6	0.0 —	8.5 —	— —
Mn	0.104	0.0 —	2.3 —	— —	0.0 56.5	0.5 55.5	— 55.0
Ni	0.082	0.0 38.3	9.0 47.0	— 38.0	0.0 —	8.0 —	— —

* Excitation source: 40 kV, 15 mA.

nickel are shown in Table 7. Similarly, uran was separated from thorium in the presence of EDTA with Alizarine Blue, and uran in thorium was also determined [19]. Further, this precipitation-separation technique was applied to the indirect determination of phosphorus and chlorine[20]. Phosphorus was separated as phosphorus ammonium molybdate and chlorine as silver chloride. Then the x-ray intensities of Mo $K\alpha$ in phosphorus ammonium molybdate and of Ag $K\alpha$ in silver chloride were measured, and from these results the amounts of phosphorus and chlorine were determined. With this method phosphorus below 200 μg and chlorine below 700 μg showed the linear relation between those x-ray intensities and these amounts. The calibration curve for phosphorus is shown in Fig. 11 and the results applied to phosphorus in steels and to chlorine in sponge titanium are shown in Tables 8 and 9.

Table 8. Determination of phosphorus in steel and cast iron.*

Sample	X-ray anal.	Chemical anal.
Steel a	0.012	0.013
Steel b	0.003	0.003
Cast iron a	0.074	0.070
Cast iron b	0.077	0.071
Cast iron c	0.077	0.074

* Excitation source : 40 kV, 10 mA

Table 9. Determination of chlorine in sponge titanium.*

Sample	X-ray anal.	Chemical anal.
A	0.080	0.085
B	0.069	0.062

* Excitation source : 40 kV, 10 mA

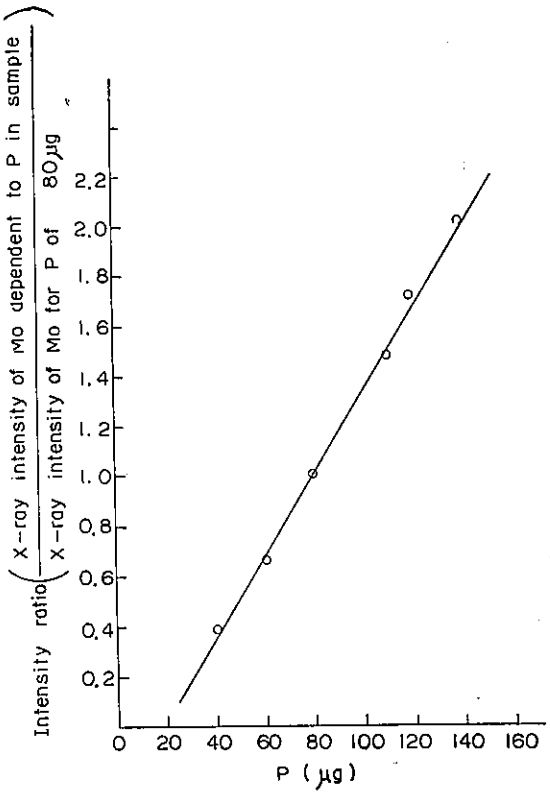

Fig. 11. Calibration curve for P.

Table 10. Simultaneous determination of composition and thickness of nickel-iron alloy films on copper.

Sample	Composition (w_{Fe})		Thickness X-ray (μ)
	Chem. anal.	X-ray anal.	
A	0.153	0.151	0.103
B	0.210	0.206	0.056
C	0.106	0.0864	0.094

3. Simultaneous determination of alloy film thickness and its composition, and the effect of backing metals[22][18][23]

The simultaneous determination of alloy film thickness and its composition which had not hitherto been examined[22] was studied. Here the results on the permalloy film (Ni 80 per cent Fe 20 per cent alloy evaporated or plated on copper plate) will be described. To measure the film thickness, two method were studied.

(22) K. Hirokawa, T. Shimanuki and H. Gotô, Z. anal. Chem., **190** (1962), 309.
(23) K. Hirokawa, M. Suzuki and H. Gotô, Z. anal. Chem., **199** (1964), 89.

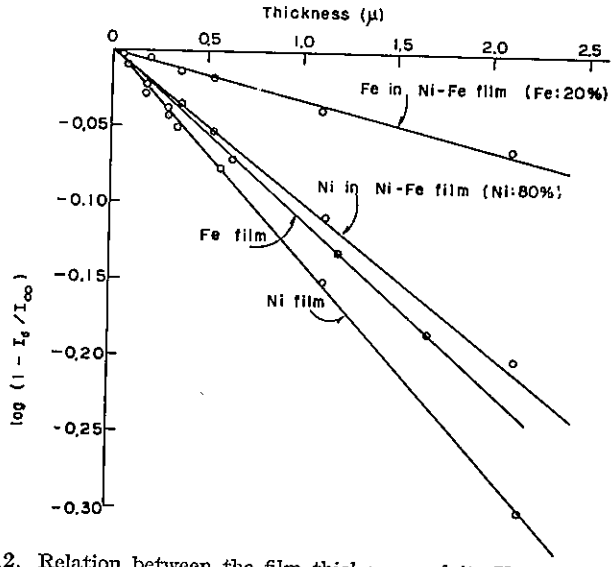

Fig. 12. Relation between the film thickness and its X-ray intensity

One was to measure the x-ray intensity of the element in film itself and the other was to measure the x-ray intensity of the element in the backing material through the film.

In the present report, the former method will be described, and first the relation between x-ray intensities of iron and nickel in nickel, iron and nickel-iron alloy (Ni: 80 per cent, Fe: 20 per cent) film and the thickness of these films below 3 μ is shown in Fig. 12. It was also recognized that when the film thickness was constant, a linear relation was realized between the x-ray intensity and its composition near the concentration range of about 80 per cent nickel. Then the experimental equation for the simultaneous determination of alloy film thickness and its composition was obtained as follows:

$$(0.282 - 0.39\, w_{Fe}) \cdot \log\left(1 - \frac{I_d}{I_\infty}\right)_{Fe} = (0.39\, w_{Fe} + 0.008) \cdot \log\left(1 - \frac{I_d}{I_\infty}\right)_{Ni}$$

$$\log\left(1 - \frac{I_d}{I_\infty}\right)_{Fe} = -\,0.434\,(0.39\, w_{Fe} + 0.008)\, d\,, \tag{8}$$

where w is the weight fraction, I_d the x-ray intensity of nickel or iron in film, I_∞ the x-ray intensity of nickel or iron in these bulk metals and d the film thickness. The results obtained by applying this method is shown in Table 11. When the film thickness was below 0.1μ the following simple relationship was obtained.

$$\left(\frac{I_d}{I_\infty}\right)_{Fe} = (0.397\, w_{Fe} + 0.005)\, d$$

$$\left(\frac{I_d}{I_\infty}\right)_{Ni} = (0.306 - 0.507\, w_{Fe})\, d \tag{9}$$

Table 11. Application results of the equations (8) and (9) to the same sample.

Equation	Composition (w_{Fe})	Thickness (μ)
(8)	0.181	0.073
(9)	0.184	0.073

Table 12. Wave lengths of the absorption edge of the element to be excited and wave lengths of the characteristic X-ray of elements to excite those elements.

Element to be excited	Wave length of absorption edge (Å)	Element to excite	Wave length of charact. x-ray (Å)	Element to be excited	Wave length of absorption edge (Å)	Element to excite	Wave length of charact. x-ray (Å)
Mg	(K) 9.517	Al (Kα)	8.337	Ge	(K) 1.117	Se (Kα)	1.105
Al	(K) 7.951	Si (Kα)	7.125	Sr	(K) 0.770	Nb (Kα)	0.746
Cl	(K) 4.397	K (Kα)	3.741	Y	(K) 0.728	Mo (Kα)	0.709
K	(K) 3.437	Ca (Kα)	3.358	Zr	(K) 0.687	Ru (Kα)	0.643
Ca	(K) 3.070	Sc (Kα)	3.031	Mo	(K) 0.620	Rh (Kα)	0.613
Sc	(K) 2.758	Ti (Kα)	2.748	Ag	(K) 0.486	Sb (Kα)	0.470
Ti	(K) 2.497	Cr (Kα)	2.290	Sn	(K) 0.425	Cs (Kα)	0.400
V	(K) 2.269	Mn (Kα)	2.102	Ce	(L) 2.164	Eu (Lα)	2.212
Cr	(K) 2.070	Fe (Kα)	1.937			Mn (Kα)	2.101
Mn	(K) 1.896	Co (Kα)	1.789	W	(L) 1.215	Te (Lα)	1.207
Fe	(K) 1.743	Ni (Kα)	1.658			As (Kα)	1.176
Co	(K) 1.608	Cu (Kα)	1.541	Pb	(L) 0.950	U (Lα)	0.911
Ni	(K) 1.483	Zn (Kα)	1.435			Sr (Kα)	0.875
Cu	(K) 1.380	Ga (Kα)	1.340	Th	(L) 0.761	Nb (Kα)	0.746
Zn	(K) 1.283	Ge (Kα)	1.254	U	(L) 0.722	Mo (Kα)	0.709

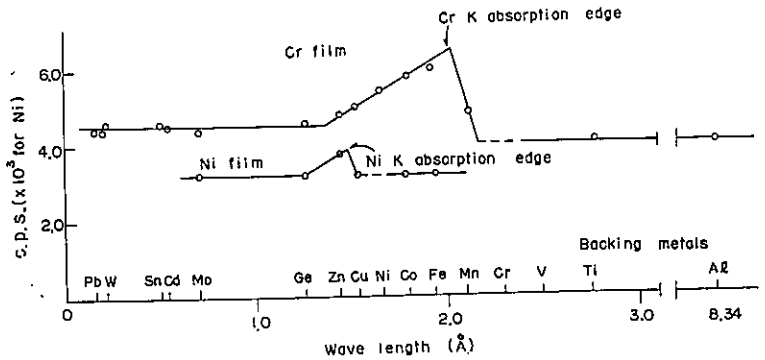

Fig. 13. Effect of backing metals on the X-ray intensity of the element in film.

The results obtained by applying Eqs. (8) and (9) are shown in Table 11. In the simultaneous determination of alloy film thickness and its composition, the influence of the element in backing materials must be taken into account. This effect may be called the absorption edge effect[23]. For example, with nickel film

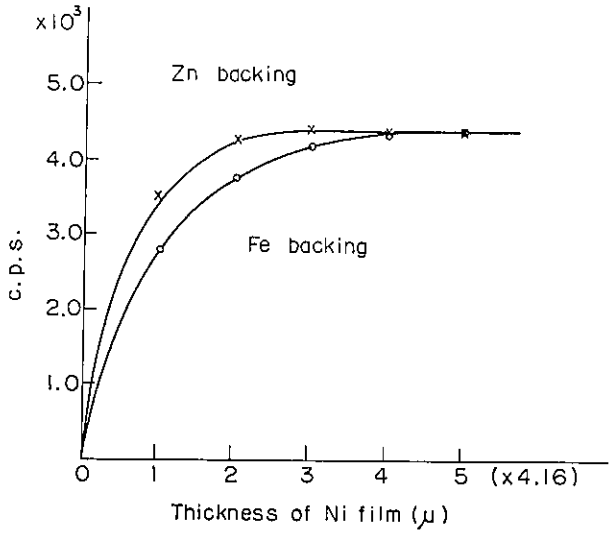

Fig. 14. Relation between metal film thickness and its backing metal.

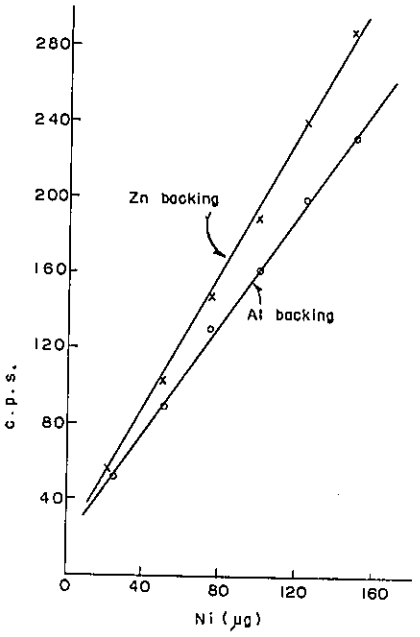

Fig. 15. Increasing of sensitivity of small amounts of Ni according to backing metal.

of ca. 5μ thickness and chromium film, the variations of x-ray intensities with various backing metals were studied, and these results are shown in Fig. 13. This phenomenon could also be observed not only with metal films but also with organometallic precipitate or filter paper, on which sample solution was dried up. This phenomenon, of course, could not be observed with thick films over infinite

thickness (for Ni over about 20 μ), and the example for nickel is shown in Fig. 14. On the other hand, it was possible to increase the sensitivity of the determination of element in organometallic precipitates or in thin films[23]; for example, the difference in the calibration curve for nickel in organometallic precipitate between aluminium backing metal and zinc backing metal is shown in Fig. 15. This phenomenon, of course, can be observed in all elements from the principle of the x-ray excitation, and the examples of this phenomenon are shown in Table 12. From this table it can easily be seen that it is effective to use chromium or titanium target to excite light elements, and that a small amount of iron in zinc can be determined non-destructively with high sensitivity.

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